

## DC ELECTRICAL CONDUCTIVITY OF IODINE DOPED TETRAPYRAZINO VANADYL OXIDE

ASAWER SALIMTUMMA

Chemistry Department, College of Education for Pure Sciences, University of Basrah, Basrah, Iraq

### ABSTRACT

*Tetrapyrazinoporphrazine Vanadyl oxide complex was synthesized. A thin surface film from the complex was casted on glass substrate, and its dc electrical conductivity was measured. The film was then doped with an iodine vapor, and its dc electrical conductivity was measured. The electrical measurement shows that the iodine doped thin film has higher conductivity than the undoped, due to the oxidation of the porphrazine complex.*

**KEYWORDS:** Tetrapyrazino Porphrazine Vanadyl Oxide, Doping & Electrical Properties

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### INTRODUCTION

Due to the interesting electronic and optical properties, Tetrapyrazinoporphrazine (Pz) also called azaphthalocyanines (AzaPc), have potential applications as biomedical agents, chemical sensors, liquid crystals and non-linear optical materials <sup>(2, 3)</sup>.

Porphyrins have recently gained increasing attention. This is due to strong correlation between the nature of the electronic and optical properties of the macro cyclic ring system, and the substituent (peripheral and central metallic) elements <sup>(2)</sup>.

The Azaphthalocyanines show good solubility in organic solvent, compared to phthalocyanine complexes <sup>(4)</sup>. In another hand, and due to the extended  $\pi$ -conjugated system in phthalocyanine and Azaphthalocyanines, they exhibit a high tendency for aggregation, which causes the decrease of solubility and difficulty of purification, characterization, broadening of Q-band and the low ability to generate the singlet oxygen, which is the active agent in photodynamic therapy(PDT) <sup>(5)</sup>. The dc electrical studies show its semiconducting properties.

Doping of phthalocyanines and semiphthalocyanines is well known as a mean of decreasing resistance. Doping could be carried out by many doping agents such as halogens, quinones and their derivatives <sup>(6)</sup>, AsF<sub>5</sub> <sup>(6)</sup>, XeF<sub>2</sub> <sup>(7)</sup> and others <sup>(8)</sup>.

In this work, a complex of Tetrapyrazinoporphrazines vanadyl oxide (PzVO) was prepared and doped with Iodine vapor and their dc electrical conductivities were measured and characterized by CHN analysis and IR, UV- Visible spectroscopy. : Preparation of the compounds

- **Preparation of Dicyanopyrazine <sup>(9)</sup>, DCP:** A mixture of 1 ml (2.18 mmol) of Glyoxal, 2ml ethanol and 25 drops of acetic acid was added to a conical flask containing of 2.36 gram (0.0218 mol) of Diamino malonitrile (DAMN) soluble in 25 ml of ethanol. The reaction mixture was refluxed for four hours and then left for two days. The solid precipitate was filtered and recrystallized from (1:1) mixture of Hexane

and Acetone and filtered again. The product is Pale yellow crystalline solid with a yield of 1.6 gram (56.21%). Mp: 133-135<sup>0</sup>C. CHN, calculated (C<sub>6</sub>H<sub>2</sub>N<sub>4</sub>): C: 55.33, H: 1.53, N: 43.24 Found C: 54.48, H: 1.26, N: 42.24. The preparation reaction is shown in figure 1.

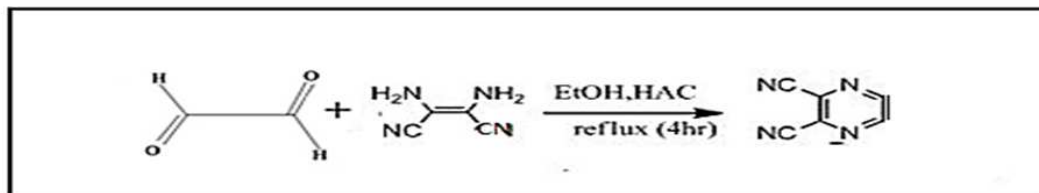


Figure 1: Preparation of DCP

- Preparation Tetrapyrazinoporphrazine Vandy, PzVO (IV):** 0.52 g (4 mmol) of DCP was dissolved in 10 ml DMF in a round bottomed flask containing 0.253 g (1mmol) of hydrated Vanadyl sulfate (VOSO<sub>4</sub>.5H<sub>2</sub>O). Then, 0.24 g of urea was added to the mixture and, the reaction mixture was refluxed for two hours with magnetic stirring. The reaction mixture was then cooled, filtered and then dissolved in 10 ml of chloroform, and the mixture then purified by adding the mixture drop-wise, by stirring in a beaker containing 100 ml of ethanol. The solid product then filtered and the purification process was repeated three times. The product is a pale Bronze powder with a yield of (0.38 g, 64.72%). Decomposition temperature is 237-239 <sup>0</sup>C. CHN calculated (C<sub>24</sub>H<sub>8</sub>N<sub>16</sub>VO) C: 49.07, H: 1.36, N: 38.16; Found C: 49.98, H: 1.31, N: 37.13. The reaction is shown in figure 2

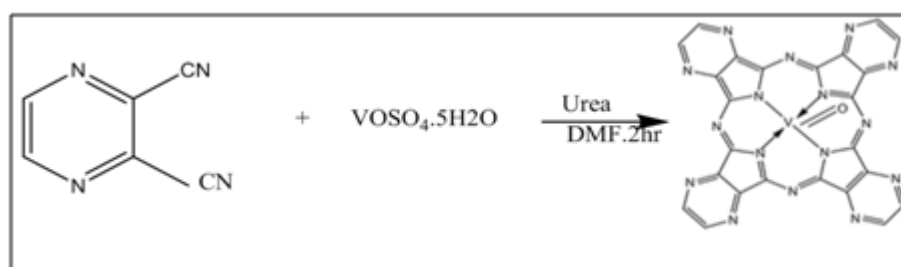


Figure 2: Preparation of PzVO

### The Spectral Analysis

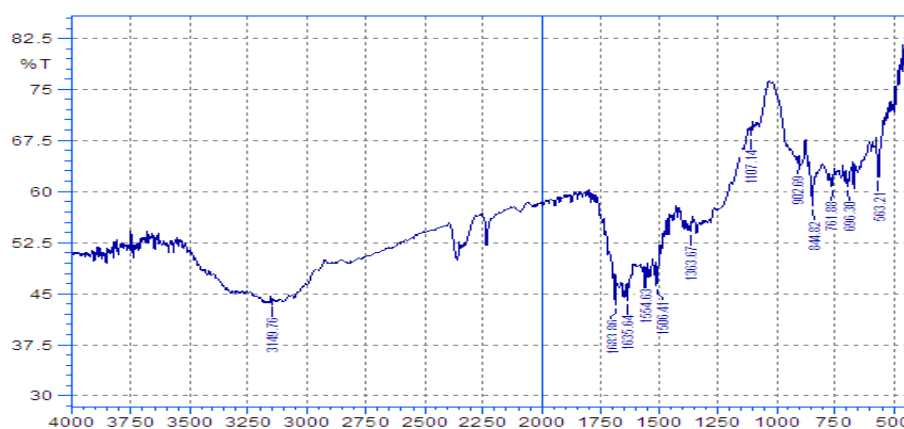
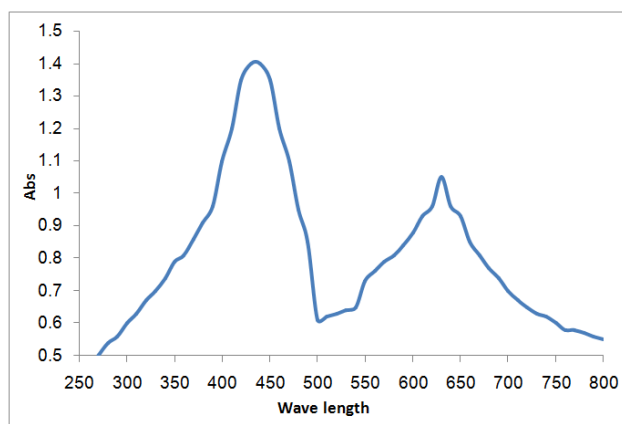


Figure 2: The IR spectrum of PzVO (KBr disc)

**IR:** The disappearance of the nitrite peak at  $2240\text{ cm}^{-1}$  is the most characteristic of C-H, stretching at  $3149\text{ cm}^{-1}$  and the C=N stretching at  $1683\text{ cm}^{-1}$ .

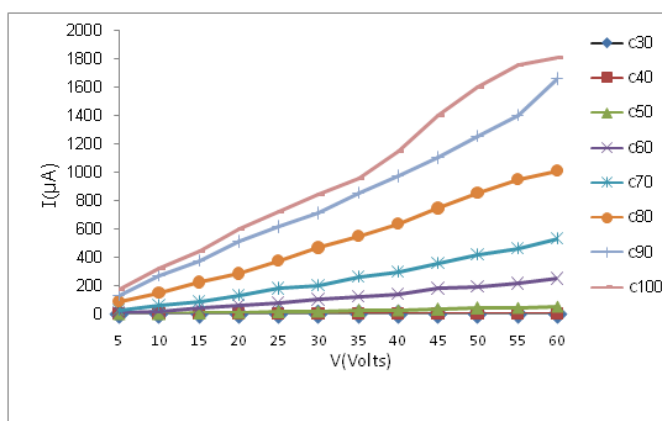


**Figure 3: The Electronic Spectrum of PzVO (in DMF,  $25^{\circ}\text{C}$ )**

**The Electronic Spectrum of the Complex, PzVO:** Figure 3 shows the characteristic (Soret) band at 425 nm, due to,  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$ , and Q band at 625 nm, which is due to,  $\pi\text{-}\pi^{*(1,11)}$  and weak d-d of the central metal atom included inside the  $\pi\text{-}\pi^*$  band. Due to the insolubility of the complex in most of the known solvents and to prevent aggregation, we used DMF as solvent.

### Electrical Properties

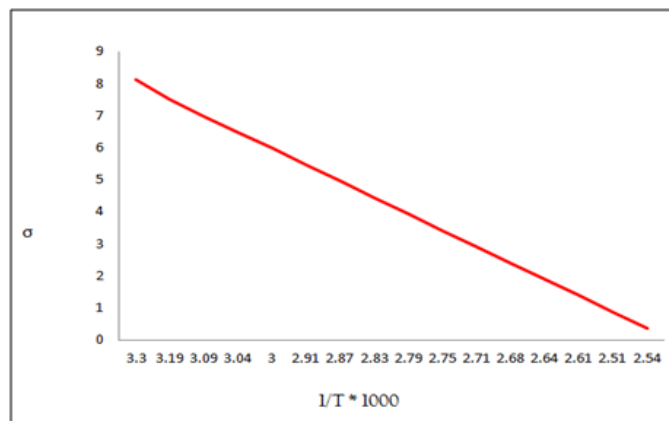
**Preparation of the Samples:** The samples were prepared as thin films, casted on glass substrate. The aluminum electrodes were evaporated on the glass substrates ( $2 \times 0.5\text{ cm}^2$ ) wrapped with copper wire ( $0.0325\text{ cm}$  diameter) in the middle of the substrate. The cell constant is ( $0.5\text{ cm}^{-1}$ ). The samples were doped in an iodine vapor in a closed vessel for one day, with covering the electrodes. Then, the cells were dried in an oven at  $100^{\circ}\text{C}$ . The dc electrical conductivity is measured in cryostat supplied with variable heating element and cell electrode holder connected to a cell containing variable voltage supply, voltmeter and ammeter <sup>(12)</sup>



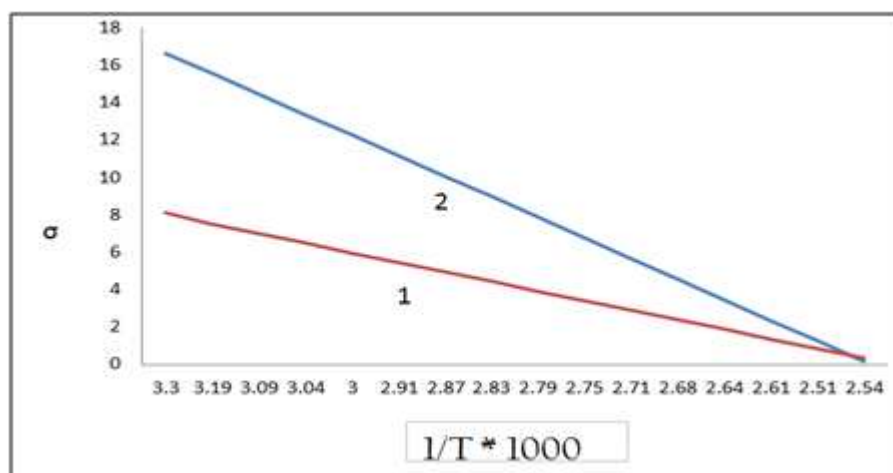
**Figure 4: The I/V Curve at Different Temperatures for PzVO**

Figure 4 shows the V/I curve for the complex PzVO at different temperatures and voltage range from 5-60 volts. It shows the ohmic relation, especially at lower voltages, where there is no space charge limited current. Figures 5 show the relationship between dc conductivity and the reciprocal temperatures at different temperatures, and, under voltage of 7

volts for PzVO. Figure 6 shows the electrical conductivity for both doped and undoped PzVO. The graph shows higher dc conductivity of the doped in comparison to the undoped. The induced conductivity of PzVO is due to the oxidation of the complex by the Iodine ( $I_2$ ) to form  $I^{-3}$  and  $I^{-5}$  reduced structures<sup>(13, 14)</sup>. The relationship between dc conductivity and the reciprocal temperature was drawn according to the Arrhenius equation,  $\ln \sigma = \ln \sigma_0 - \frac{\Delta E}{kT}$ , where  $\sigma$  and  $T$  dc conductivity and absolute temperature respectively are,  $\sigma_0$  is the pre-exponential factor,  $k$  is Boltzmann constant ( $8.61733 \times 10^{-5} \text{ eV/K}$ ) and  $\Delta E$  is the activation energy.  $-\frac{\Delta E}{k}$  is the slope of the straight line. From the slopes, we calculate the activation energy in eV. The measured voltage was 7 volts to ensure that, there is no space limited current. The activation energies of both undoped and doped PzVO are 1.9 and 0.8 eV, respectively.



**Figure 5: The Relationship between  $\ln \sigma$  (Ln Dc Conductivity) and Reciprocal Absolute Temperature for the Vanadyl Complex (Pzvo)**



**Figure 6: The Relationship between  $\ln \sigma$  (Ln Dc Conductivity) and Reciprocal Absolute Temperature for both Undoped (A) and Doped (B) Vanadyl Complex (Pzvo)**

## CONCLUSIONS

The Tetrapyrazine vanady oxide complex could be doped by Iodine vapor and the dc-electrical conductivity is higher than the undoped

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## REFERENCES

1. J. Simon and J. J. Andr'e; "Organic Semiconductors" John and Willy, London (1985).
2. E. Gonca., Highly symmetrical polyfluorinated porphyrazines., "J. fluorochem", 149, 65-71 (2013).
3. J. M. Fox.; T.J. Katz.; S, Van Elshocht.; T, Verbiest.; M, Kauranen.; A. Persoons.; T.; Krauss, T. Th. Chang.; and L. Brus.; J. Am. Chem. Soc. 121, 3453-3459(1999).
4. M. P. Donzello, C. Ercolani and P. A. Stuzhin, "Coordination Chemistry Reviews", 250, 1530 (2006).
5. M. Kostka., P. Zimcik., M. Miletin., P. Klemra., K. Kopecky and Z. Musil., "J. photochem. Photobiol, A-Chem" 178, 16-25(2006).
6. G. Briebleb, Angew. Chem. Int. Ed., 3, 617(1964).
7. D. Djurado, A. Hamwi, J. C. Cousseins, Synth. Mat., 22, 109(1985).
8. D. Djurado, C. Fabre, A. Hamwi, and J. C. Coussein, Synth. Mat., 22, 93. (1987).
9. N. A. Hussein, International Journal. of Semiconductor Science and Technology, 5, 2278(2015).
10. R. M. Silverstein and F. X. Webster, "Spectroscopic Identification of Organic Compounds", 6th Ed, John Wiley and Sons, Inc., New York (1996).
11. A. M. Shaffer, M. Gouterman and E. R. Davidson, Teor. Chem. Acta, 30, 9(1979).
12. N. A. Hussein and Raheem K. Zobon, International Journal of Applied and Natural Sciences, 3, 2319(1914).
13. G. A. Cox and P. C. Knight, J. Phys. Chem. Solids, 34, 1655(1973).
14. N. A. Hussein, PhD Thesis, Nottingham University, UK (1990).

